

Surface Active Agents From Isopropenyl Esters: Acylation of Isethionic Acid and N-Methyltaurine¹

3597

R.G. BISTLINE, JR., E.S. ROTHMAN, S. SEROTA, A.J. STIRTON² and A.N. WRIGLEY,
Eastern Regional Research Laboratory,³ Philadelphia, Pennsylvania 19118

Abstract

Acylation of sodium isethionate with isopropenyl stearate at 200 C for 30 min gave a 95% yield of sodium 2-sulfoethyl stearate, acetone being the only byproduct. Acylation of N-methyltaurine at 200 C for 90 min gave a 95% yield of N-methyl-N-(2-sulfoethyl) stearamide sodium salt. Corresponding surface active derivatives were also prepared from pelargonic, lauric, myristic, palmitic, oleic, phenylstearic and hydrogenated tallow fatty acids from their respective isopropenyl esters. Detergency, foam height, wetting time, lime soap dispersing power, critical micelle concentration and other surfactant properties were evaluated. Optimum properties were found at the C₁₄-C₁₈ fatty acid chain length. Unsaturation or branching increased solubility. The 2-sulfoethyl esters were similar to the N-methyl-N-(2-sulfoethyl) amides in foam height, wetting ability and lime soap dispersing power, superior to the N-methyl-N-(2-sulfoethyl) amides in detergency, but inferior in calcium stability and less stable to acid and alkali. Both compounds are readily biodegraded. The fatty isopropenyl ester synthesis has an advantage in yield and purity of the product and could increase the utilization of the 2-sulfoethyl esters and N-methyl-N-(2-sulfoethyl) amides in many applications.

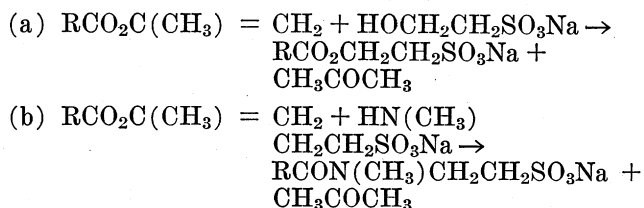
Introduction

In the early 1930's, I.G. Farbenindustrie researchers reported the synthesis of surfactants by means of the fatty acylation of sodium isethionate and N-methyltaurine which were marketed under the trade names "Igepon A" and "Igepon T" (1-3). A variety of procedures, designed to reduce time and production costs, have been proposed for the preparation of the 2-sulfoethyl esters: (a) The reaction of a fatty acid chloride with sodium isethionate (1,4,16). (b) The reaction of a fatty acid and sodium isethionate (5,1). (c) The reaction of a fatty acid with carbyl sulfate (1). (d) The reaction of sodium salt of a fatty acid with chloroethanesulfonic acid salts (1). (e) The reaction of chloroethyl ester of a fatty acid with sodium sulfite (6). (f) The reaction of a fatty acid anhydride with sodium isethionate, using boric acid catalyst (7).

Fewer methods for the preparation of N-methyl-N-(2-sulfoethyl) amides have been reported: (a) The reaction of fatty acid chloride with an aqueous solution of N-methyltaurine (2,8). (b) The direct condensation of a fatty acid with N-methyltaurine at 220-260 C (9).

Despite the many methods of synthesis, the cost of the 2-sulfoethyl esters and the N-methyl-N-(2-sulfoethyl) amides has not been reduced sufficiently to capture an important share of the household market.

In earlier work of this laboratory (10,11) the fatty isopropenyl esters were found to be effective and convenient agents for replacing the active hydrogen atoms of alcohols, amines, amides and imides with fatty acyl groups. It was decided therefore to test the suitability of fatty isopropenyl esters for the preparation of 2-sulfoethyl esters and N-methyl-N-(2-sulfoethyl) amides as follows:



Although more than 50 patents have been granted in the past 40 years on the preparation and applications of the 2-sulfoethyl esters and N-methyl-N-(2-sulfoethyl) amides relatively few data on pure compounds have been published. A second objective was therefore to provide a survey of the physical and surface-active properties of these compounds. In the present work, pelargonic, lauric, myristic, palmitic, stearic, oleic, phenylstearic and hydrogenated tallow fatty acids were converted to the 2-sulfoethylesters and N-methyl-N-(2-sulfoethyl) amides and evaluated for Krafft point, surface and interfacial tension, critical micelle concentration, rates of hydrolysis, detergency, foam height, calcium stability, wetting ability, metallic ion stability and lime soap dispersing power.

Experimental Procedures

Materials

Commercial grade pelargonic, lauric, myristic, palmitic, stearic and oleic acids were purified to 96% minimum purity by fractional distillation. Phenylstearic acid was purchased from Barlow Chemical Co., Ossining, New York, and contained a mixture of C₆-C₁₇ position isomers. Wilmar hydrogenated tallow fatty acid, obtained from Wilson-Martin Co., Philadelphia, Pa., was composed of stearic (64.6%), oleic (1.3%), palmitic (29.7%), myristic (4.0%) and lauric (0.2%) acids. Purified propyne was supplied by Airco Industrial Gases, Riverton, New Jersey. Sodium isethionate, supplied by GAF Corporation, New York, was dried azeotropically with benzene. The percent ash calculated as Na₂SO₄ for C₂H₅O₄SNa was 47.93; found: 47.92 N-methyltaurine sodium salt, received as a 35% aqueous solution from GAF, was dried azeotropically with benzene and then recrystallized from 95% ethanol. The per cent ash calculated as Na₂SO₄ for C₃H₈NO₃SNa was 44.05; found: 43.93.

Isopropenyl Ester Preparation

The isopropenyl esters are readily synthesized by the addition of propyne to carboxylic acids under pressure, using the zinc fatty acid salt as catalyst. Details of the preparation and physical constants

¹ Presented at the ISF-AOCS Meeting in Chicago, September 1970.

² Deceased.

³ E. Mark. Nutr. Res. Div., ARS, USDA.

for the products will be the subject of a forthcoming paper (12).

Acylation

Sodium 2-Sulfoethyl Stearate (Sodium 2-Hydroxyethanesulfonate Stearate (Ester) or Stearic Ester With Sodium 2-Hydroxyethanesulfonate). A mixture of 0.075 moles isopropenyl stearate, 0.093 moles sodium isethionate and 0.001 moles *p*-toluenesulfonic acid was heated at 200 C in a Wood's metal bath for 30 min in the apparatus shown in Figure 1. Acetone vapor, the only by-product, began to form within the first minute. Unreacted isopropenyl stearate was acetone-extracted from the cooled reaction product. The 2-sulfoethyl ester, which contained sodium isethionate, was obtained in 95% crude yield, and was subsequently crystallized three times from 50% ethanol to produce a white crystalline product in 78% yield. Analysis: Calculated for $C_{26}H_{39}SO_5Na$: C, 57.94; H, 9.48; S, 7.73; Na, 5.55. Found: C, 57.74; H, 9.50; S, 7.74; Na, 5.47.

Sodium N-Methyl-N-(2-Sulfoethyl) Stearamide (N-Methyl-N-Stearoyltaurine Sodium Salt). A mixture of 0.075 moles isopropenyl stearate, 0.092 moles N-methyltaurine sodium salt and 0.001 moles *p*-toluenesulfonic acid was caused to react at 200 C for 90 min in the apparatus shown in Figure 1, producing a 95% crude yield of sodium N-methyl-N-(2-sulfoethyl) stearamide and N-methyltaurine. Acetone appeared 17 min after the reaction flask was immersed in the bath. The product was crystallized three times from 50% ethanol to produce a white crystalline material in 70% yield. Analysis: Calculated for $C_{21}H_{42}NSO_4Na$: C, 58.98; H, 9.90; N, 3.28; S, 7.50; Na, 5.38. Found: C, 58.66; H, 10.06; N, 3.06; S, 7.66; Na, 5.40.

Elemental analyses were determined for the other five chemical individuals of each type. Range of deviation from theory for the 2-sulfoethyl esters was: C, .30 to .50; H, .05 to .25; S, .04 to .34; Na, .01 to .05. Range of deviation for the N-methyl-N-(2-sulfoethyl) amides was: C, .10 to .40; H, .04 to .41; N, .10 to .30; S, .07 to .44; Na, .01 to .09.

Hydrolysis Studies

Acid hydrolysis was measured in 100 ml hot distilled water solutions, containing 0.005 moles HCl and 0.005 moles 2-sulfoethyl ester or N-methyl-N-(2-sulfoethyl) amide. Temperature was maintained at 60 C and 100 C. Ten-milliliter samples were withdrawn, diluted with 75 ml of neutralized 95% ethanol, and titrated with 0.1 N NaOH at suitable intervals,

using phenolphthalein indicator. Separate titration of same strength of *n*-valeric acid with equal molar amounts of N-methyltaurine, sodium salt, showed that the amine did not effect the phenolphthalein end point (pH 10.0 in alcohol) or interfere with the accuracy of the acid titration. Amount of reaction, *x*, was determined from the increase in acidity, and first order kinetics were calculated according to the equation $k_1 = 1/t \cdot \ln a/(a-x)$. Time for 50% hydrolysis was determined from the $\log(a-x)$ vs. *t* plot.

Alkaline hydrolysis was measured at 60 C and 100 ml hot distilled water solutions, containing 0.005 moles NaOH and 0.005 moles of 2-sulfoethyl ester or N-methyl-N-(2-sulfoethyl) amide. Samples of 10 ml were withdrawn and titrated at intervals, with 0.1 N HCl, using phenolphthalein indicator. Second order kinetics were calculated, according to the equation $k_2 = 1/t \cdot x/a \cdot (a-x)$. Time for 50% hydrolysis was determined from the $1/(a-x)$ vs. *t* plot.

Physical and Surface Active Properties

Melting points were determined on the Fisher-Johns apparatus. The Krafft point was measured by gradually heating a 1% dispersion until it became a clear solution. Surface tension and interfacial tension at the petrolatum-water interface were measured on 0.1% distilled water solutions with the du Noüy tensiometer. The critical micelle concentration (cmc) was measured by the pinacyanole chloride titration (13).

Foam heights were determined on 0.25% solutions of active ingredient in distilled water and 0.05% active ingredient plus 0.20% builder in 300 ppm hard water using the Ross-Miles Foam Test (14). Detergency, the average of 10 measurements, was measured as the increase in reflectance, ΔR , after washing 10 swatches of standard soiled cotton in the Terg-O-Tometer for 20 min at 60 C and 110 cycles/min. The Draves Cotton Skein Test (15) used a 5 g cotton skein with a 3 g hook on 0.1% distilled water solutions to determine wetting ability. The surfactants' tolerance for calcium ion was measured by the calcium stability test (16). The lime soap dispersion test (17) measured the ability to disperse the insoluble soaps formed in hard water. Metallic ion stability (18) was determined by titrating 1% salt solutions (Ca^{++} , Mg^{++} , Cu^{++} , Al^{+++} , Ba^{++} , Fe^{++} , Pb^{++} , Zn^{++} and Ni^{++}) into 1% solutions of sodium 2-sulfoethyl oleate and sodium N-methyl-N-(2-sulfoethyl) oleamide, until solutions became turbid. The metallic ion stability (18) was recorded as 10 times the number of milliliters of added 1% metal salt solution which produced turbidity in 10 ml of 1% surfactant solution. If the surfactant tolerated 10 ml of 1% metal salt solution, it was rated as 100.

Results and Discussion

The 2-sulfoethyl esters were readily prepared by the reaction of the fatty isopropenyl esters with sodium isethionate at 200 C with isopropenyl stearate for example, heating for 10, 20 and 30 min afforded crude yields of 89%, 91% and 95%, respectively.

In the preparation of sodium N-methyl-N-(2-sulfoethyl) stearamide, acetone did not appear for 17 min, owing to an induction period. Previous work (19) demonstrated that *p*-toluenesulfonic acid was necessary to acylate amines. Reaction times of 45, 60 and 90 min resulted in 88%, 94% and 95% crude yields.

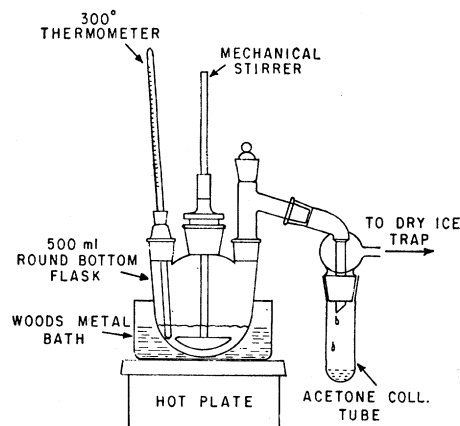


FIG. 1. Apparatus for the reaction of isopropenyl esters of fatty acids with sodium isethionate and N-methyltaurine.

TABLE I
Physical Properties of 2-Sulfoethyl Esters and N-Methyl-N-(2-Sulfoethyl) Amides

Sodium salt	Melting point, °C	Krafft point, °C	Surface (ST) and interfacial tension (IT), 0.1%, 25 °C dynes/cm		Critical micelle concentration (13), mmoles/liter
			ST	IT	
2-Sulfoethyl					
pelargonate	240-242	< 0	51.4	24.3	42.4
laurate	216-218	30	46.6	20.7	6.4
myristate	191-193	39	37.6 ^a	9.5 ^a	2.0
palmitate	176-177	51	36.7 ^a	8.8 ^a	Insoluble
stearate	169-170	59	35.1 ^a	7.8 ^a	Insoluble
oleate	146-148	< 0	36.0	5.2	0.23
phenylstearate	Amorphous	< 0	35.6	5.2	0.09
tallowate	147-149	56	33.8 ^a	7.0	Insoluble
N-Methyl-N-(2-sulfoethyl)					
pelargonamide	224-225	< 0	61.0	37.7
lauramide	207-208	< 0	49.6	24.5	8.7
myristamide	201-203	23	41.0	13.6	1.82
palmitamide	187-188	43	40.4	12.0	0.43
stearamide	171-173	58	37.8	10.3	Insoluble
oleamide	162-164	0	39.3	10.9	0.29
phenylstearamide	Amorphous	< 0	32.0	9.4	0.16
tallowamide	163-165	50	37.9	10.5	Insoluble
Oleyl sulfate	124-125	< 0	35.8	7.4	0.29
Methyl α -sulfoate	175-176	39	39.7	8.4	0.16

^a Measured at 35 °C.

Physical properties are recorded in Table I. Melting points decreased with increasing molecular weights for both the 2-sulfoethyl esters and N-methyl-N-(2-sulfoethyl) amides. As a result of high Krafft points, surface and interfacial tensions of some of the 2-sulfoethyl esters were determined at 35 °C. Derivatives of pelargonic acid had high surface and interfacial tension values as well as high cmc values, indicating that they are simple ions rather than colloidal electrolytes. Surface and interfacial tension values as well as cmc for the others decreased with increasing molecular weight and were similar to those of the alkyl sulfates and esters of α -sulfofatty acids. All of the compounds are soluble in 95% and absolute ethanol but insoluble in chloroform, toluene and hexane.

Surfactant properties are reported in Table II. The values for the pelargonate derivatives are atypical for detergents. Foaming ability and detergent values increased as the hydrocarbon chain lengthened to C₁₄-C₁₈. The 2-sulfoethyl esters and N-methyl-N-(2-sulfoethyl) amides were equal in foam height and wetting ability. The 2-sulfoethyl esters were better detergents, but the N-methyl-N-(2-sulfoethyl) amides were superior in calcium stability and lime soap dispersing power. High detergency values and good lime soap dispersion suggest that the 2-sulfoethyl esters and N-methyl-N-(2-sulfoethyl) amides might be effective in mixtures with soap and other surfactants. Results of Table III show

that both types compounds exhibit synergism in combination with sodium methyl α -sulfoate (NaMea-ST), linear alkylbenzenesulfonate and soap. Values of 100 indicating good ion stability were found for Mg⁺⁺, Cu⁺⁺, Al⁺⁺⁺, Fe⁺⁺, Zn⁺⁺ and Ni⁺⁺ in both types of compounds. Each was sensitive to Ca⁺⁺, Ba⁺⁺ and Pb⁺⁺. Values of 26, 20 and 36, respectively, were determined for sodium 2-sulfoethyl oleate; 68, 28 and 60, respectively, for sodium N-methyl-N-(2-sulfoethyl) oleamide. Times for 80% biodegradation of 5 ppm solutions by the "River Water Die Away" test (20), were 19 hr for the 2-sulfoethyl esters and 62 hr for the N-methyl-N-(2-sulfoethyl) amides. These values approximate those of the alkyl sulfates, i.e., sodium oleyl sulfate, 26 hr, and are less than those of esters of α -sulfofatty acids, i.e., sodium methyl α -sulfoate, 93 hr.

Acid and alkaline hydrolysis rate constants, together with the time required for 50% hydrolysis, are listed in Table IV. Hydrolysis of the 2-sulfoethyl esters at 80 °C and 100 °C in either acid or alkali was too rapid to measure. These values indicate the greater stability of the N-methyl-N-(2-sulfoethyl) amides compared to the 2-sulfoethyl esters.

The present work demonstrates the advantages of the isopropenyl ester method of synthesis. It provides high yields in short reaction times with acetone as the only by-product. The 2-sulfoethyl esters and N-methyl-N-(2-sulfoethyl) amides are obtained as white powders and free of inorganic salts. Through the

TABLE II
Surfactant Properties of 2-Sulfoethyl Esters and N-Methyl-N-(2-Sulfoethyl) Amides

Sodium salt	Foam height (14)		Detergency				
	60 °C, 0.25%, Dist. H ₂ O	mm, 0.05% + 0.1% NTA + 0.1% builder, 300 ppm	60 °C, 0.25%, Dist. H ₂ O	ΔR , 0.05% + 0.1% builder, 300 ppm	Wetting time (15), 0.1%, 25 °C, sec	Calcium stability (16), ppm	Lime soap dispersing power (17), %
2-Sulfoethyl							
pelargonate	60	47	29.4	27.5	>300	>1800	90
laurate	233	165	34.9	28.1	10	410	13
myristate	219	200	33.4	33.3	15	320	9
palmitate	223	220	33.6	38.9	25 ^a	300	7
stearate	194	183	38.9	40.3	>300 ^a	280	9
oleate	215	210	33.5	39.3	21	1700	9
phenylstearate	169	125	44.2	42.1	>300	>1800	10
tallowate	210	193	37.0	39.1	61 ^a	620	10
N-Methyl-N-(2-sulfoethyl)							
pelargonamide	43	43	26.8	26.8	>300	>1800	90
lauramide	193	165	29.3	27.6	49	>1800	7
myristamide	225	210	33.0	30.7	16	>1800	3
palmitamide	192	213	30.6	32.3	36	>1800	6
stearamide	190	163	31.9	34.2	98	>1800	6
oleamide	220	212	31.9	32.0	24	>1800	6
phenylstearamide	164	153	38.9	35.1	>300	>1800	13
tallowamide	205	193	29.7	33.5	59	>1800	6

^a Determined at 35 °C.

TABLE III
ΔR^a Values, Detergent Mixtures, 800 ppm H₂O, 60 C

Component A	0.05% A + 0.02% builder ^b	Component B	
		2-Sulfoethyl stearate, sodium salt	N-Methyl-N-(2-sulfoethyl) stearamide, sodium salt
		0.025% A + 0.025% B + 0.1% NTA + 0.1% builder	
Sodium hydrogenated tallow alcohol sulfate	42	43	42
Sodium methyl α-sulfotallowate	30	35	33
Linear alkylbenzene-sulfonate	31	36	33
Soap from tallow fatty acids	27	40	37

^a ΔR, increase in reflectance after washing.

^b Builder, 55% Na₅P₃O₁₀, 24% Na₂SO₄, 10% Na₄P₂O₇, 10% Na Metasilicate, 1% carboxymethyl cellulose.

TABLE IV
Rate Constants, Acid and Alkaline Hydrolysis

Sodium salts	Temperature, C	0.005 M HCl		0.005 M NaOH	
		k ₁ ^a	t _{1/2} ^b min	k ₂ ^c	t _{2/2} ^d min
2-Sulfoethyl stearate	60	0.045	15	0.35	65
	100	e	e	e	e
N-Methyl-N-(2-sulfoethyl) stearamide	60	0.00038	1100	f	f
	100	0.00024	280	<0.00002	>1000

^a k₁ (first order reaction), 1/t · ln a/(a-x) (min⁻¹).

^b t₁, time for 50% acid hydrolysis.

^c k₂ (second order reaction), 1/t · x/a(a-x) [liters/(mole) (min)].

^d t₂, time for 50% alkaline hydrolysis.

^e Too rapid to measure.

^f Too small to measure.

acceleration of the reaction rates and purity of products, the isopropenyl ester synthesis might effect a cost reduction, thus increasing the use of these types of surfactants in the textile and detergent industries. The advantages of this method should also be applicable in the preparation of other types of surfactants, such as derivatives of ethylene glycol, diethanolamine, glycine, sarcosine and protein hydrol- yzate.

ACKNOWLEDGMENT

The determination of elemental analyses was made by Laverne Scroggins and Annette Kravitz.

REFERENCES

1. Daimler, K., and K. Platz (I.G. Farbenindustrie), U.S. Patent 1,881,172 (1932).
2. Guenther, F., F. Munz and H. Haussman (I.G. Farbenindustrie), U.S. Patent 1,932,180 (1933).
3. Hoyt, L.F., Pb 3868, Office of Technical Services, U.S. Dept. of Commerce, Washington, D.C., 1945.
4. Schenck, L.M. (General Aniline and Film Corp.), U.S. Patent 3,004,049 (1961).
5. Anderson, R.J., and L.M. Schenck (General Aniline and Film Corp.), U.S. Patent 2,923,724 (1960).
6. Schwartz, A.M., and J.W. Perry, "Surface Active Agents," Vol. 1, Wiley-Interscience, New York, 1949, p. 94-102.
7. Schenck, L.M. (General Aniline and Film Corp.), U.S. Patent 2,898,352 (1959).
8. Kastens, M.L., and J.J. Ayo, Jr., Ind. Eng. Chem., 48:1626-1638 (1950).
9. Burnette, L.W., and M.E. Chiddix (General Aniline and Film Corp.), U.S. Patent 2,880,219 (1959).
10. Rothman, E.S., JAOCS 45:189-193 (1968).
11. Rothman, E.S., S. Serota, T. Perlstein and D. Swern, J. Org. Chem. 27:3123-3127 (1962).
12. Rothman, E.S., and S. Serota, JAOCS, 48:373-375 (1971).
13. Corrin, M.L., H.B. Kleven and W.D. Harkins, J. Chem. Phys. 14:480-486 (1946).
14. Ross, J., and G.D. Miles, Oil Soap 18:99-102 (1941).
15. Draves, C.Z., and O.L. Sherburne, Amer. Dyest. Rep. 39:771-772 (1950).
16. Wilkes, B.G., and J.N. Wickert, Ind. Eng. Chem. 29:1234-1239 (1937).
17. Borghetty, H.C., and C.A. Bergman, JAOCS 27:88-90 (1950).
18. Harris, J.C., ASTM Bull. 141:49-53 (1946).
19. Rothman, E.S., S. Serota and D. Swern, J. Org. Chem. 29: 646-650 (1964).
20. Weil, J.K., and A.J. Stirton, JAOCS 41:355-358 (1964).

[Received January 15, 1971]